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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Sintered Body Comprising a Catalytic Metal

We VARTA AKTIENGESELLSCHAFT, A German Company, of Neue Mainzer Strasse 54, Frankfurt/Main, Germany. do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a porous sintered body comprising a catalytic metal which when containing adsorbed hydrogen is sensitive to atmospheric oxygen and therefore loses all or at least part of its catalytic activity during storage.

It is known to protect catalysts which are sensitive to atmospheric oxygen by storing them after their manufacture or activation under a liquid, for example under water, an alkali solution, an alcoholic solution, a liquid hydrocarbon or oil. In this connection, it has previously been reported that such catalysts have been introduced into liquids which solidify upon cooling. Paraffin wax and higher fatty alcohols have been named.

In a recent proposal, catalysts sensitive to air, and particularly Raney metal catalysts, are preserved or protected by impregnation with an alcohol which is soluble in water or caustic alkali solution and which is substantially non-volatile and liquid at room temperature, after which the excess alcohol is removed; in this manner, even pulverulent catalyst material can be stored in the atmosphere after its preservation.

However, it has meanwhile been found that the handling of catalysts thus treated presents difficulties upon subsequent use or treatment. The complete removal of the preservative is not simple; it is particularly the active sites of the catalysts which are blocked by residual traces of the preservative. It is also impossible for catalysts from which the preservative has been removed to be treated or to be manipulated in the usual manner, since their sensitivity to air or oxygen is restored after removal of the preservative. This disadvantage is particularly evident when the catalyst is to become a constituent part of an electrode.

Thus, for example, it has hitherto been impossible to introduce into electrode skeletons activated Raney metal catalysts, or metal catalysts obtained by thermal decomposition in a reducing atmosphere, without danger and without irretrievable loss of their catalytic properties.

In the copending Application No. 28771/66 (Serial No. 1,108,706) there is provided a method of treating hydrogen-transfer catalysts in such manner that they lose their sensitivity to atmospheric oxygen but can nevertheless be reactivated in a simple manner upon subsequent treatment. The method comprises the step of removing the adsorbed hydrogen from the catalyst by means of a substance capable of chemical reaction with hydrogen. The treated catalyst is reactivated before use by reintroducing hydrogen into it.

It has been found that treatment with peroxide compounds and with organic nitro compounds is particularly suitable for removing the hydrogen without harmful effect upon the subsequent activity of the catalyst. Other oxygen-containing compounds, such as chromic acid and nitric acid and their salts, are also suitable.

It is also known to deactivate catalysts by electrochemical conversion of the hydrogen contained in them. In practice, this process is, however, only suitable for solid, electrically

[*Price 4s. 6d.*]

conductive bodies comprising hydrogenation catalyst.

In industry it is, however, of particular importance that the powder used as the raw material in the manufacture of the catalyst bodies should be catalytically inactive in the period during which the powder is processed.

It is also much easier to convert a fine powder into a catalytically active substance than a solid body produced from such powder. Furthermore, the mechanical strength of the solid body is substantially reduced by the procesess of activation and reactivation because the catalyst particles undergo changes in volume during these processes. In this connection, it may also be noted that dissolving or leaching and impregnating processes are facilitated and can be carried out considerably more quickly with powders than with porous bodies.

In the method of the said copending Application for the deactivation of hydrogen-transfer catalysts it was found that it was possible to produce from the inactivated powder by cold-pressing catalyst bodies in the form of foil which for a short time were useful gas-consuming electrodes, and useful in low-pressure fuel cells and electrodialysers after having been charged electrochemically or chemically, with hydrogen. Owing to their inadequate mechanical stability, the reactivated catalyst bodies are unsuitable for electrolysis and for use as negative electrodes in accumulators provided with an alkaline electrolyte. It was found in these tests that the full original degree of catalytic activity was not attained and the strength of the cold-pressed bodies was inadequate for technical requirements. One has always attempted to produce the catalysts required for reactions at temperatures ranging, for example, between −30°C and +150°C, at the lowest possible temperature. The higher the temperature employed in the manufacture, the more readily defects in the lattice will heal or be remedied by recrystallisation. One has therefore deliberately refrained from damaging the specific structure of the catalyst by the supply of heat.

In the tests which, for these reasons, were carried out with great hesitation, it has, however, been found unexpectedly that sintered bodies which are insensitive to oxygen and which can, after being recharged with hydrogen, be re-used as hydrogen-transfer catalysts (i.e., as hydrogenation or dehydrogenation catalysts) in chemical and electrochemical processes, particularly in fuel cells, are obtained from catalyst powders known to be effective in hydrogen-transfer reactions carried out at temperatures below 200°C., when the total hydrogen is withdrawn from the active sites of such powders.

The term "catalytic metal" as employed hereinafter denotes a metal effective as a hydrogen-transfer catalyst, that is, as a hydrogenation or dehydrogenation catalyst.

According to the invention therefore, there is provided a method for the manufacture of a porous sintered body comprising a catalytic metal (as hereinbefore defined) which when containing adsorbed hydrogen is both effective as a hydrogen-transfer catalyst at a temperature below 200°C and sensitive to air, in which said catalytic metal in pulverulent form and containing adsorbed hydrogen is treated to remove the adsorbed hydrogen and is thereafter moulded with the application of pressure and heat to form the porous sintered body. The catalytic metal is advantageously embedded in a supporting skeleton made of a different material, so that the mechanical strength of the sintered body may be substantially increased whilst valuable catalytic material is economised.

The invention makes it possible to produce porous sintered bodies containing the catalytic metal and of high mechanical strength, which bodies can be stored for long periods of time.

The method according to the invention is applicable not only to Raney metals, for example nickel, cobalt and iron, and to alloys of Raney metals which are sensitive to air and oxygen, but to any hydrogen-transfer catalyst metal which is active to relatively low temperatures and pressures, including, for example, metals of the platinum group. Examples of the alloys of Raney metals which may be used are those obtained from the usual Raney alloys to which from 0.1 to 10% by weight of titanium, chromium or vanadium has been added. Such alloys are, for example, described in detail in Austrian Patent Specification No. 206,867. Further, platinum black and palladium black in quantities of 0.01 to 0.5% by weight may be deposited on a supporting material, such as carbon, barium sulphate, aluminium oxide or diatomaceous earth. The method according to the invention may also be applied to nickel obtained by decomposition of nickel formate, nickel carbonate, nickel oxalate, or nickel hydroxide; nickel chromite; to a precipitate consisting of cobalt and a small amount of thorium and containing diatomaceous earth as supporting material, as well as nickel boride and mixed nickel borides of the kind described in German Auslegeschrift No. 1,202,255.

As compared with the known double skeleton catalyst electrodes described in German Patent Specification No. 1,019,361, the porous sintered bodies produced according to the invention afford the advantage that they may contain a considerably higher proportion of the catalytic metal while at the same time meeting the condition of uniform strength. Where formerly, 1.2 parts by weight of carbonyl nickel had for example to be mixed with one part by weight of Raney

nickel alloy (nickel content 43% by weight), it is now possible to use one part by weight of Raney nickel (nickel content 100%) to one part by weight of carbonyl nickel. The range of reactions in the electrochemical conversion of gases and liquids is thereby considerably increased, and the danger of poisoning is substantially reduced. In the former method of production there occurs during the sintering or hot-pressing the disadvantageous reaction that the aluminium migrates from the alloy granules rich in aluminium into the material of the supporting skeleton, that is the carbonyl nickel in the example given, so that the Raney nickel is deprived of its inactive constituent. After this process, the Raney alloy and the carbonyl nickel material of the supporting skeleton form considerable quantities of NiAl, an alloy or compound from which the aluminium cannot be leached to give Raney nickel. Further, it is particularly the electrochemically important zones in the pores of the electrodes which are blocked by this process. Electrodes comprising a porous sintered body produced according to the invention and containing a Raney metal as the catalytic metal and a supporting skeleton such as nickel, are distinguished by the fact that the supporting skeleton cannot combine with the inactive constituent of the Raney alloy during the hot-pressing step since such inactive constituent is not present, the catalytic metal being already present in Raney form and not as a Raney alloy.

An additional advantage afforded in the production of these electrodes resides in the fact that the catalytic metal is separated from the inactive constituent of the Raney alloy before the sintered body is manufactured. The advantages with respect to time and material resulting from the fact that the inactive constituent can be removed from Raney alloy powders with a solvent within 30—100 minutes according to their particle size, will be readily appreciated upon considering that the same treatment of a sintered body 4 mm in thickness takes 6 to 10 days even when carried out at elevated temperature and in the presence of a material which forms a soluble complex with the inactive constituent so as to ensure that the inactive constituent does not obstruct pores in the sintered body. When the metal used for the metallic powder in the supporting skeleton is the same as that used for the catalytic metal, for example carbonyl nickel as supporting nickel and Raney nickel as catalytic metal, bodies of high mechanical stability which do not crack or burst even at twice the pressures which cause cracks in the known double skeleton electrodes (DSK electrodes), are obtained upon sintering and hot-pressing.

A substantial improvement may be obtained by covering part of the surface of the catalytic metal particles with a promoter, such as copper, mercury, cadmium or silver, during its manufacture and before the catalytic metal is formed into the porous sintered body. Such promoters can be deposited uniformly over part of the surface of the pulverulent catalytic metal. The promoters improve the resistance of the Raney metal to deactivation, for example by heat or poisoning, and during reactivation of the catalyst, are effective to accelerate the incorporation of substantial quantities of hydrogen and to reduce the time required for the reactivation. Moreover, the addition of the aforementioned doping agents or promoters enables the electrodes to recover quickly from their collapse. In sintered bodies obtained by the method according to the invention the promoter is distributed evenly in the subsequently catalytically active layer of the electrode, this being in contrast with the distribution of a promoter introduced into preformed electrodes.

The pulverulent catalytic metal may be mixed with a powder of a material which can be and is removed from the sintered body after moulding. Such powder, which functions as a pre-forming filler and so enhances the formation of pores, may be used in an amount of 5—40% by weight and may be of a particle size of 0.01—1.5 mm. Such pore-forming filler may be of a kind which can be dissolved out of the sintered body with the evolution of hydrogen or it may be of a kind which can be dissolved out without the evolution of gas, for example, an alkali metal carbonate or alkali metal chloride. The pore-forming filler may also consist of or comprise a substance, for example ammonium carbonate or citric acid, which volatilises with or without decomposition when the pulverulent catalytic metal is subjected to sintering or hot-pressing.

The withdrawal or removal of adsorbed hydrogen from the catalytic metal particles may be effected as described in the copending Application No. 28771/66 (Serial No. 1,108,706). Alternatively and/or in addition, soluble compounds of bromine and iodine in which the bromine and iodine have a valency of more than one may be used for such purpose, particularly towards the end of the process of hydrogen removal. Water-soluble iodates are particularly suitable for this purpose.

In the technical literature, the chlorates or hypochlorites have hitherto been referred to as the strongest poisons for hydrogenation catalysts. Thus, for example, Patisson and Degering (J.Am. Chem. Soc. 73, 611, 1951) have found that it is the chlorine compounds which have the strongest inhibiting effect upon Raney catalysts. The hydrogenation of styrene is stopped completely even by minute quantities of chlorine (0.03 grams per kg. of substance to be hydrogenated). Chlorides which during the removal of the hydrogen from the

catalyst are formed by reduction of chlorine compounds resulting from the strongly reducing hydrogen, are known to be strong catalyst poisons.

It has surprisingly been found that the adsorbed hydrogen may also be removed from the catalytic metal by alkaline solutions of oxygen-containing chlorine compounds, for example chlorates or hypochlorites, which readily give off oxygen. Thus in the method according to the invention the pulverulent hydrogen-transfer catalytic metal may be treated with a solution of an oxygen-containing chlorine compound which readily gives off oxygen, to remove the adsorbed hydrogen, after which the powder, if necessary or desired after having been mixed with a powder by which the mechanical strength of the subsequent sintered body is increased and/or with a powdered pore-forming filler, is moulded with the application of pressure and heat to produce the desired body.

The use of chlorine-containing compounds does not affect the catalytic activity of the porous sintered body thus obtained.

The sintered body produced from the powders, particularly when used as an electrode in a fuel cell, is, however, rather inactive upon being put into operation for catalytic purposes, and have to be recharged with hydrogen.

It has been found, according to the invention, that the reactivation of the catalyst is greatly facilitated by treating it with hydrogen at elevated temperature, advantageously above 50°C and preferably within the range 60—90°C.

Catalysts and catalyst bodies made of nickel or containing nickel have been examined particularly closely. It has been found that the original degree of activity is not restored by using a hydrogen-yielding agent or gaseous hydrogen for the recharging.

Curves 1, 2 and 3 plotted in Figure 2 of the accompanying drawings which relate to a hydrogen electrode produced according to the invention having a covering layer consisting of 2 grams of light carbonyl nickel and a catalytically active working layer containing 18 grams of a mixture of one part by weight of deactivated Raney nickel part of the surface of which had copper deposited on it in finely divided form in the manner hereinafter described in Example 9, 1.3 parts by weight of light carbonyl nickel powder and 0.1 part by weight of aluminium powder of a very fine particle size. The Raney nickel present in the working layer was one which had been deactivated with an aqueous potassium iodate solution (in the manner hereinafter described in Example 9) before admixture with light carbonyl nickel and aluminium powders and subsequent hot-pressing to form the electrode. Before being used in a half-cell, the electrode was treated with a concentrated caustic potash solution in order to dissolve out the aluminium with the evolution of hydrogen. Upon operation of the electrode under a hydrogen pressure of 1.4 atmosphere gauge, curve 1 was obtained with the electrolyte at a temperature of 20°C., curve 2 was obtained with the electrolyte at a temperature of 40°C., and curve 3 was obtained with the electrolyte at a temperature of 60°C. The shape of curve 3, which indicates that the electrode is not improved by the increased operating temperature alone is particularly striking.

Figure 3 of the accompanying drawings illustrates this even more clearly. The electrode tested in this instance also contained Raney nickel from which hydrogen has been removed with the aid of potassium iodate before the Raney nickel and the light carbonyl nickel powder had been mixed and sintered to produce the working layer. The electrode proper, which was produced by the hot-pressing method (0.5 tons/450°C) contained 2 grams of light carbonyl nickel powder forming the covering layer, a gas-conducting layer produced from a mixture of one part by weight of potassium chloride and three parts by weight of light carbonyl nickel powder being provided on the opposite side of the working layer. This electrode was also tested in a half-cell system; the electrolyte consisted of 6-normal KOH, the hydrogen pressure being 1 atmosphere gauge. Curves 1a, 2a, and 3a of Figure 3 were plotted from data obtained at 20°C., 40°C. and 60°C. respectively. When the electrode was operated at 80°C, however, the results obtained, plotted as curve 4, were in complete contrast to those previously obtained and plotted in curves 1a, 2a and 3a and indicated that the electrode had extraordinarily good electrochemical properties. Surprisingly, it was moreover found that when the electrode was again subjected to load at temperatures of 18°C., 40°C., and 60°C., the voltage characteristics showed a considerable improvement as compared with the first three measurements, this being shown by curves 1b, 2b, and 3b respectively.

Repeated experiments have meanwhile revealed that in the de-activated nickel catalysts the incorporation of hydrogen required for restoring the original degree of activity takes place only at elevated temperatures, particularly at temperatures between 60°C and 80°C.

Figure 4 of the accompanying drawings shows the sintered catalytic bodies thus reactivated retain their high degree of activity even when they are subjected to load for long periods of time. An electrode of a construction very similar to that of the electrodes hereinbefore described with reference to Figurs 5 and 6 was operated for a period of 936 hours at 60°C. under a hydrogen pressure of 1 atmosphere gauge and under a

load of 100mA/sq. cm. At position I of the curve plotted in Figure 4, the electrode holder, which still contained air, was flushed with hydrogen. At position II the electrode holder had to be re-tightened as a short circuit occurred at the electrode. In the interval between II and III the calomel reference electrode was replaced. At position IV, the endurance test was interrupted in order to enable the equilibrum rest potential, that is the open circuit potential, to be measured. At position V the test was interrupted for an extended period of time since the supply of hydrogen failed. The operation of the electrode in the endurance test was continued for more than 3000 hours without deterioration of the potential.

Figure 5 of the accompanying drawings shows the current-voltage characteristic of an electrode in which the covering layer consisted of 2 grams of light carbonyl nickel powder, and the catalytically active working layer consisted of 18 grams of an intimate mixture of 1 part by weight of pre-activated copper-plated (that is, chemically plated with copper) Raney nickel (particle size 10—15μ) preserved with potassium iodate, and 1.3 parts by weight of light carbonyl nickel powder. The Raney nickel over part of the surface of which copper had been deposited in finely divided form, was produced in the manner hereinafter described in Example 9. The preservation step, that is the removal of adsorbed hydrogen, with potassium iodate was also carried out as described in that Example.

The electrode was formed under a pressure of 0.5 tons/sq.cm. at a temperature of 450° C.

The electrolyte consisted of an aqueous 6 normal caustic potash solution having a temperature of 80°C. The operating pressure of the hydrogen gas was 1 atmosphere gauge and a saturated calomel electrode was used as a reference electrode. As the electrode was subjected to increasing load (current density), it was found that the potential of the electrode improved steadily as from the moment a value of 50 mA/sq.cm. was reached.

The current-voltage characteristics of two electrodes according to the invention are plotted in Figure 9 of the accompanying drawings. In electrode *a* the covering layer consisted of 2 grams of light carbonyl nickel powder, the catalytically active working layer consisted of 13 grams of an intimate mixture of 1 part by weight of preactivated copper-plated Raney nickel preserved with potassium iodate (particle size 10—15 μ; copper content 0.25%), and 1.3 parts by weight of light carbonyl nickel powder. The Raney nickel was produced as hereinafter described in Example 9, its treatment with potassium iodate also being carried out as described in that Example.

The covering layer of electrode *b* consisted of 2 grams of light carbonyl nickel powder, whereas the working layer consisted of the same material as that used in electrode *a* except, however, that it contained 0.1 part by weight of aluminium powder of a particle size of 10—15 μ.

Both electrodes were produced by the hot-pressing method under a pressure of 0.5 tons/sq. cm. at a temperature of 440°C.

After the pressing electrode *b* was treated for one hour with hot 6-normal caustic potash solution to remove the aluminium powder.

Both electrodes were then operated in aqueous 6-normal caustic potash solution at 13° to 14°C. under a hydrogen pressure of 1 atmosphere gauge. Curves 5a and 5b correspond to the first values obtained with electrodes *a* and *b*. Curves 6a and 6b indicate the values at 14°C. after a preliminary treatment with an aqueous 6-normal caustic potash solution at a temperature of 80°C.

The aluminium powder had been added to the active material of the electrode *b* on the assumption that the electrode would be activated even by the hydrogen evolved upon dissolution of the aluminium to such an extent as to make a subsequent incorporation of hydrogen at higher temperatures impossible. A comparison between curves 5b and 6b shows, however, that this assumption was true only to a limited extent.

The invention is illustrated in the following examples.

Example 1

500 grams of a Raney alloy (50% by weight of nickel, the remainder being aluminium) of a particle size of 10—15 μ were carefully introduced into cold 6-normal KOH. The solution contained 10 grams of potassium sodium tartrate per litre as a complex former for the aluminium dissolved out of the alloy. In those tests in which copper served as promoter, 1.25 grams of copper (II)—chloride dihydrate ($CuCl_2.2H_2O$) were gradually added with vigorous stirring after the initial vigorous evolution of hydrogen was complete, and the copper in a very finely divided state formed deposits over part of the surface of the Raney nickel particles. The suspension was then heated to the boiling point of the caustic potash solution with continuous stirring, and the Raney nickel was not separated from the solution until the evolution of hydrogen was complete.

The Raney nickel powder was then transferred to a container and covered with a aqueous solution of 122 grams potassium iodate. The solution was stirred for 20 hours, after which no further decrease in the iodate content occurred.

After completion of the preserving process, the powder was washed in a vacuum until it was free from alkali, subjected to

suction on a frit, and dried; no evolution of heat was observed. One part by weight of the deactivated powder was mixed slowly with 1.3 parts by weight of carbonyl nickel for 24 hours in a cube-shaped mixer. (Wuerfelmischer). The mixture was compressed in a mould under a pressure of 4 tons/sq. cm. followed by sintering for 30 minutes at 550° C in a current of hydrogen. The electrode could be stored for any length of time.

EXAMPLE 2

A Raney alloy consisting of 48% by weight of nickel, 3.0% by weight of vanadium and 49% by weight of aluminium was leached with 6N KOH as described in Example 1, and then washed twice with fresh KOH for removal of the aluminate. The catalyst was then washed with six batches of distilled water, each of 5 litres, and with vigorous stirring. The wet powder was suspended in 3 litres of water. A saturated calomel electrode serving as a reference electrode was suspended in the aqueous solution and, while checking the potential, hydrogen peroxide (3% aqueous solution) was added until the original potential had been rendered more positive by 200 mV. The supernatant solution was then drawn off by suction and potassium iodate solution was added. The solution was allowed to act for 15 hours upon the Raney powder. The subsequent treatment and drying of the powder was carried out as in Example 1. The powder obtained, mixed with light carbonyl nickel powder in the same ratio as in Example 1, was transferred to a pressure mould which already contained a layer of light carbonyl nickel which was to form the covering layer of the electrode to be formed. 5 grams of a mixture of 75% by weight of carbonyl nickel and 25% by weight of potassium chloride, of a particle size of about 200—300 μ were then added. The electrode was pressure-moulded at a temperature of 450°C. and under a pressure of 0.5 tons/sq. cm. The potassium chloride was then leached out of the electrode with boiling water.

EXAMPLE 3

A fine nickel powder obtained by thermal decomposition of nickel oxalate was introduced with stirring into an aqueous solution which contained potassium bromate, and the powder was filtered off when no further drop in the $KBrO_3$ content occurred. After the washing and drying, the deactivated nickel powder was mixed with 28% by weight of active carbon and 1.5% by weight of polyethylene, and the mixture was pressure-moulded at 160°C. to produce an electrode.

Two curves are shown in Figure 1 of the accompanying drawings, curve 1 being plotted from the X-ray diagram of Raney nickel powder from which all of the hydrogen had been removed by means of hydrogen peroxide alone, and curve 2 from a corresponding diagram taken under the same conditions of a Raney nickel powder which had only been pre-deactivated by means of a hydrogen peroxide solution, the last traces of hydrogen having been removed from the nickel powder with the aid of a potassium iodate solution. A comparison between the two curves shows clearly that the peaks 1A and 1B, both indicating the presence of nickel oxide, are absent in curve 2. The peak 2A indicates, however, that the deactivated nickel is present in a substantially enlarged cubic form.

EXAMPLE 4

200 grams of a Raney nickel alloy powder having a particle size between 50 and 100 μ and consisting of 50% by weight of nickel and 50% by weight of aluminium, was introduced slowly and with cooling into 2 litres of an aqueous 6-normal potassium hydroxide solution. This process, in which the Raney nickel was activated as a result of dissolution of the aluminium, was initially accompanied by a vigorous evolution of hydrogen. When the initially vigorous evolution of hydrogen had died down and the solution heated by the reaction had cooled down completely, 50 cc. of a 1% copper (II)-chloride solution was added with vigorous stirring. The copper was deposited as a promoter on part of the surface of the Raney nickel powder. To complete the activation of the Raney nickel, boiling was continued until the evolution of hydrogen had stopped. The catalyst material was filtered off, washed with fresh caustic potash solution to remove the aluminates formed during the activation, and then washed with water. The adsorbed hydrogen was removed from the Raney nickel by adding 2 litres of a 5% potassium chlorate solution. The solution was allowed to take effect in the cold until all of the hydrogen had been removed from the Raney nickel. The fact that the concentration of chloride ion remained constant was an indication that the reaction was complete. The powder was filtered off, washed free of chloride, and re-washed with acetone. The powder thus preserved or protected was dried at 40—50°C. under reduced pressure.

A three-layer electrode was produced using a mixture of 1 part by weight of the preserved Raney nickel doped with the copper promoter, 1.3 parts by weight of light carbonyl nickel T 255 and 0.2 parts by weight of sodium carbonate (particle size less than 71 μ) to form the working layer. Light carbonyl nickel was used to provide the covering layer of the electrode, that is to say, the layer in contact with the electrolyte when the electrode is in use, whilst a mixture of 70% by weight of carbonyl nickel and 30% by weight of potassium chloride was used to form the gas-conducting layer on the other

side of the electrode. The three layers, the working layer being the intermediate layer, were hot-pressed into a composite unit at a pressure of 0.5 t./sq. cm. and at a temperature of 450°C. The salts added to produce the pores were then removed with boiling water.

EXAMPLE 5

200 grams of a mixed Raney alloy consisting of 60% by weight of aluminium, 20% by weight of vanadium and 20% by weight of nickel, the alloy being in powder form with a particle size of 40—50 μ, was activated as described in Example 4 and doped with copper. 2 litres of a 4.8% aqueous potassium chlorate solution were added for preserving purposes. After the preservation, the powder was washed until it was free from chloride, and then dried. This powder could be stored in the atmosphere without being damaged. The powder was used for the production of three-layer electrodes as described in Example 4.

EXAMPLE 6

300 grams of a mixed Raney alloy consisting of 1 atom % of aluminium, 75 atom % of iron, and 24 atom % of nickel, the alloy being in pulverulent form with a particle size of 40—53 μ, was activated as described in Example 4. A 4.8% aqueous potassium chlorate solution was used for the preservation. The powder was used for the production of a three-layer electrode as described in Example 4.

EXAMPLE 7

100 grams of a Raney nickel alloy powder of a particle size less than 2 μ and consisting of 50% nickel and 50% aluminium was activated as described in Example 4. 20 cc. of a 1% chloroplatinic acid were added for doping. After removal of the liquor, a sodium hypochlorite solution was added for removing the adsorbed hydrogen from the Raney nickel. The preservation was carried at a temperature of −5°C. Upon termination of the reaction, the powder was washed until all of the chloride had been removed, and was then dried. The powder was used for the production of a three-layer electrode as described in Example 4.

EXAMPLE 8

A nickel catalyst obtained by the reduction of nickel oxalate at 260°C. in a current of hydrogen, was cooled under hydrogen and then introduced into a 5% potassium chlorate solution and stirred therein for two hours. It was then washed until it was free from chloride and dried. The catalyst could then be stored in the atmosphere without being damaged. The powder was used for the production of a three-layer electrode as described in Example 4.

Figure 7 of the accompanying drawings shows the voltage characteristic of a two-layer hydrogen electrode as measured against a calomel reference electrode according to the electrode current at various temperatures of the electrolyte. The electrode was produced as described in Example 4 using Raney nickel which had been doped with copper and preserved with potassium chlorate, but with the omission of the gas-conducting layer. The hydrogen gas at the electrode had a pressure of 1.0 atmosphere gauge.

Figures 8 and 9 show the curves corresponding to Figure 7 for a three-layer electrode of the kind described in Examples 5 and 6.

EXAMPLE 9

500 grams of a commercial Raney alloy (50% by weight of nickel, 50% by weight of aluminium; particle size 10—15 μ) were carefully introduced into cold 6-normal KOH to which 10 grams of potassium tartrate per litre was added to form a soluble complex with the aluminium leached out of the Raney alloy. The liquor was cooled by extraneous cooling as the Raney alloy was introduced. Upon termination of the first vigorous evolution of hydrogen, 125 ml. copper (II)-chloride solution (10 grams/l $CuCl_2 . 2 H_2O$) were added with vigorous stirring, upon which copper deposited in very finely divided form on part of the surface of the Raney nickel. The suspension was then heated at the boil with continuous stirring. Upon termination of the evolution of hydrogen, the Raney nickel was first washed twice with fresh alkali lye, and then was washed with five batches, each of two litres, of distilled water. Potassium iodate solution was then added and allowed to remain until all the hydrogen had been removed from the Raney nickel. After 24 hours the supernatant solution was filtered off, the filter residue was washed repeatedly with water, and acetone was finally poured over the filter residue; it was then dried at 50°C. in vacuo. One part by weight of the Raney nickel was mixed with one part by weight of carbonyl nickel and 0.2 part by weight of boron, and the mixture was compressed under a pressure of 0.5 tons/sq. cm. at 450°C. The electrode so produced was then immersed for about 30 minutes in boiling potassium hydroxide solution during which the boron was dissolved out. The addition of boron powder had the further effect that the atmospheric oxygen which had also been trapped in the interstices, was captured. The nascent hydrogen set free when the boron was dissolved out in the alkali solution, was incorporated directly into the cracks in the Raney nickel.

The term "ton" hereinbefore employed is the metric ton, namely 1000 kg.

WHAT WE CLAIM IS:—

1. A method for the manufacture of a porous sintered body comprising a catalytic

metal (as hereinbefore defined) which when containing adsorbed hydrogen is both effective as a hydrogen-transfer catalyst at a temperature below 200°C and sensitive to air, in which the said catalytic metal in pulverulent form and containing adsorbed hydrogen is treated to remove the adsorbed hydrogen and is thereafter moulded with the application of pressure and heat to form the porous sintered body.

2. A method according to claim I, in which the pulverulent catalytic metal is moulded in admixture with a powder effective to increase the mechanical strength of the sintered body.

3. A method according to claim 2, in which the said powder is a metal.

4. A method according to claim 3, in which the metal powder is nickel powder.

5. A method according to any one of the preceding claims, in which the particles of the pulverulent catalytic metal are covered in part with a promoter.

6. A method according to claim 5, in which the promoter is applied during the step of removing adsorbed hydrogen from the pulverulent catalytic metal.

7. A method according to claim 5 or claim 6, in which the promoter is copper, mercury, silver or cadmium.

8. A method according to any one of claims 5 to 7, in which the promoter is applied by chemical precipitation.

9. A method according to any one of the preceding claims, in which at least part of the adsorbed hydrogen is removed from the pulverulent catalytic metal by means of a soluble bromine or iodine compound in which the valency of the bromine or iodine is more than one.

10. A method according to claim 9, in which an oxy acid or bromine or iodine or a salt of such acid is used.

11. A method according to claim 10, in which a soluble iodate is used.

12. A method according to any one of claims 1 to 8, in which at least part of the adsorbed hydrogen is removed from the pulverulent catalytic metal by means of a solution of an oxygen-containing chloride compound which readily yields oxygen.

13. A method according to claim 12, in which the chloride compound is a chlorate.

14. A method according to any one of claims 9 to 13, in which the compound of bromine, iodine or chlorine is used at least towards the end of the step of removing adsorbed hydrogen from the pulverulent catalytic metal.

15. A method according to any one of the preceding claims, in which the pulverulent catalytic metal is moulded in admixture with a powder which can be and is removed during or after the moulding step.

16. A method according to claim 15, in which the said powder is a synthetic resin powder which is admixed with the pulverulent catalytic metal before, during or after the removal of the adsorbed hydrogen and prior to the moulding with the application of pressure and heat.

17. A method according to claim 16, in which the synthetic resin powder is electrically conductive.

18. A method according to claim 15, in which the said powder is a normally solid substance which volatilises when heated and is admixed with the said powder after the removal of the adsorbed hydrogen.

19. A method according to claim 18, in which the said substance is ammonium carbonate or citric acid.

20. A method according to claim 15, in which the said powder is a non-volatile substance which can be removed from the sintered body by dissolution in water or an aqueous solution and is admixed with the pulverulent catalytic metal after the removal of the adsorbed hydrogen.

21. A method according to claim 20, in which the said substance is a chloride or carbonate of an alkali metal.

22. A method according to any one of the preceding claims, in which a metal and/or a metalloid which preferentially absorbs oxygen and which dissolves in an acid or alkaline solution with the evolution of hydrogen, is added to the pulverulent catalytic metal before, during or after the removal of the adsorbed hydrogen.

23. A method according to claim 22, in which the metal or metalloid is magnesium, calcium, zinc boron, aluminium or silicon.

24. A method according to any one of the preceding claims, in which the pulverulent catalytic metal is a Raney metal.

25. A method according to claim 1, substantially as hereinbefore described with reference to any one of the Examples.

26. A sintered body whenever obtained by the method claimed in any one of the preceding claims.

27. A process for activating the sintered body claimed in claim 26, which comprises charging the sintered body with hydrogen at an elevated temperature.

28. A process according to claim 27, in which the activation is effected at a temperature above 50°C.

29. A process according to claim 28, in which the activation is effected at a temperature in the range 60—90°C.

30. A process according to any one of claims 27 to 29, in which the sintered body is charged with gaseous hydrogen while the sintered body is connected as an electrode under a cathodic load.

31. A process according to any one of claims 27 to 30, in which the sintered body

is subject one or more times to an anodic load during the activation.

32. A process according to any one of claims 27 to 29, in which the charging of the sintered body with hydrogen is effected in a solution in which a metal is dissolved with the liberation of hydrogen.

33. A process according to claim 27, substantially as hereinbefore described with reference to Example 9.

34. An electrode comprising the sintered body claimed in claim 26.

35. A fuel cell comprising the electrode claimed in claim 34.

36. An activated sintered body whenever obtained by the process claimed in any one of claims 27 to 33.

37. An electrode comprising the activated sintered body claimed in claim 36.

38. A fuel cell including the electrode claimed in claim 37.

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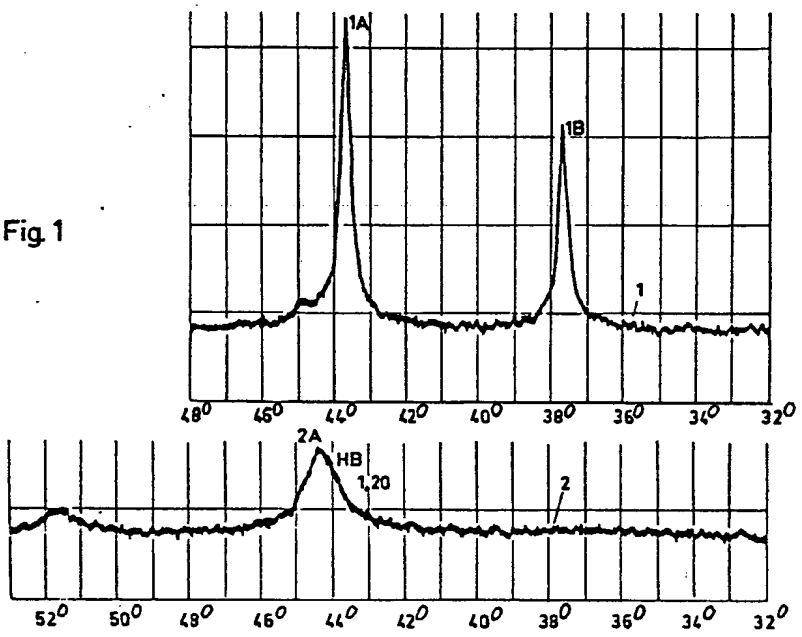
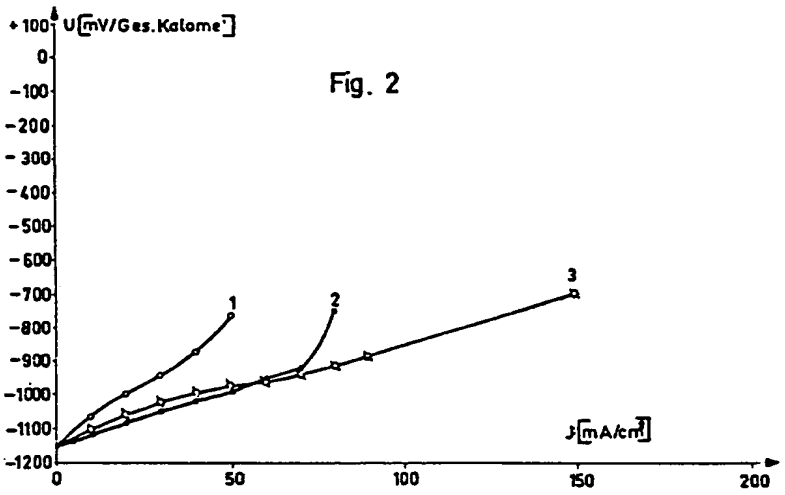
1160872 COMPLETE SPECIFICATION

5 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

Fig. 1

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-1000
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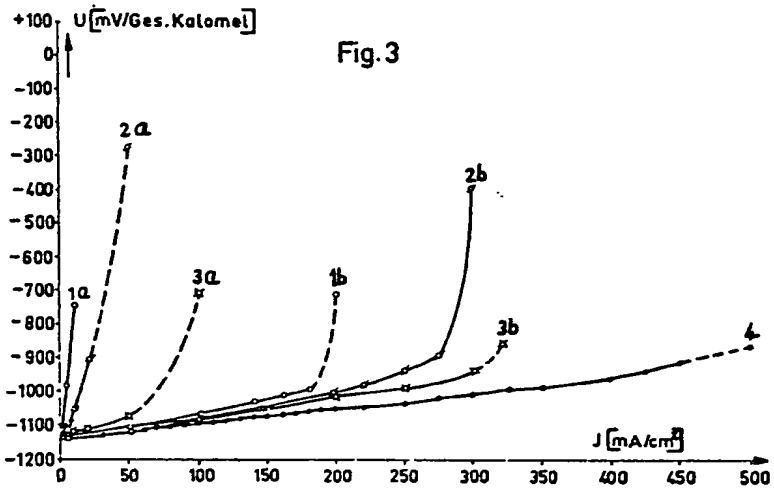
2
3
J[mA/cm²]
0
50
100
150
200

Fig. 2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-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
-1100
-1200
U[mV/Ges.Kalomel]
1a
2a
3a
1b
2b
3b
4
J[mA/cm²]
0
50
100
150
200
250
300
350
400
450
500

Fig.3

1160872 COMPLETE SPECIFICATION
5 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
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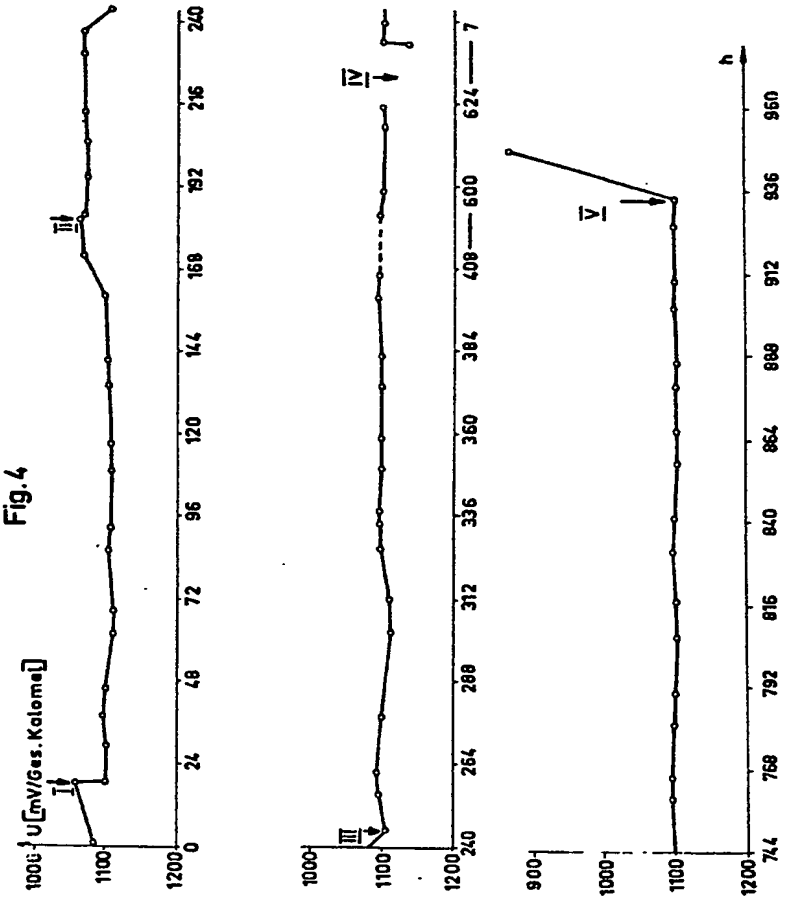

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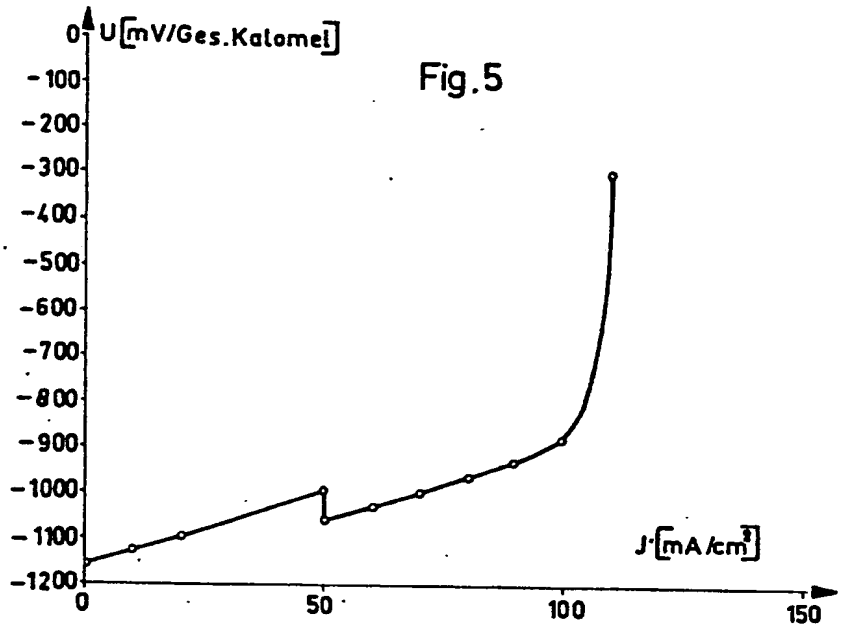
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U [mV/Ges. Kalomel]
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
-1100
-1200
0
50
100
150
J [mA/cm²]

Fig.5

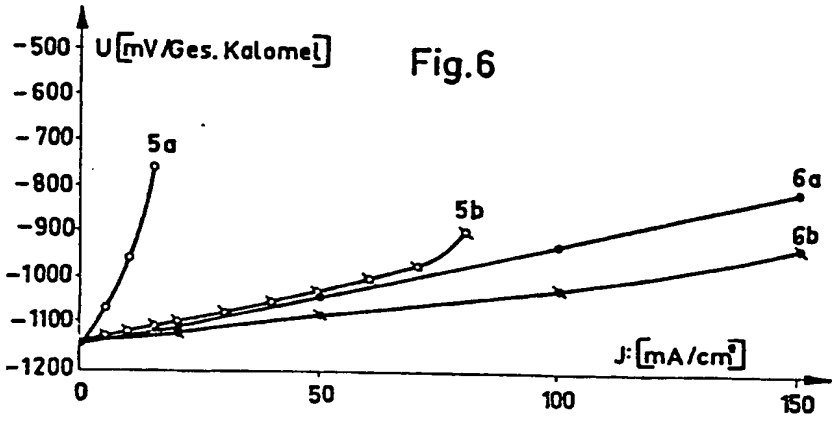
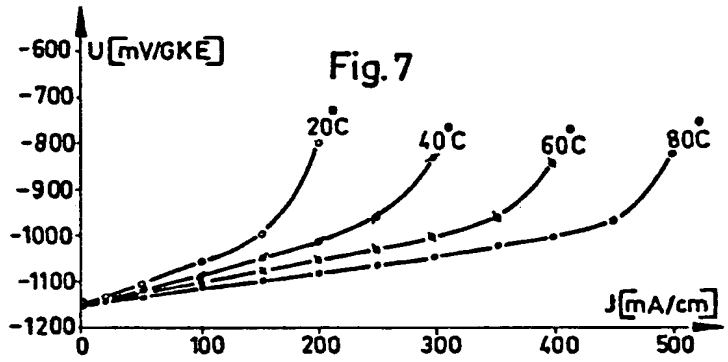

-500
U [mV/Ges. Kalomel]
-600
-700
-800
-900
-1000
-1100
-1200
5a
5b
6a
6b
0
50
100
150
J [mA/cm²]

Fig.6



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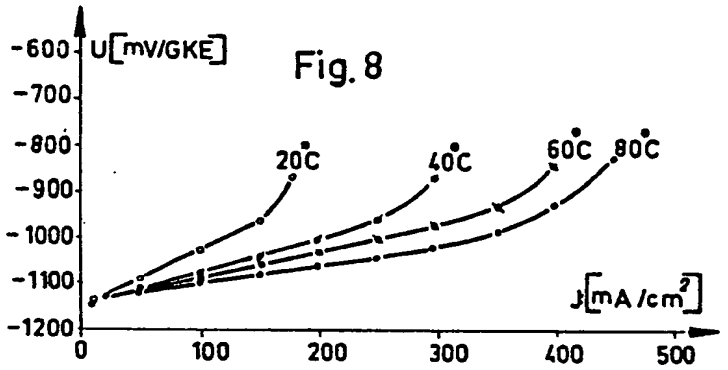

Fig. 8

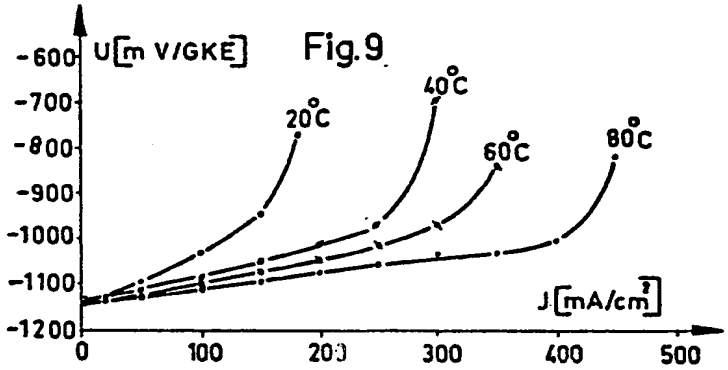

Fig. 9

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